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PAPER

Phosphido pincer complexes of platinum: synthesis, structure and reactivity†

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A series of platinum(II) complexes supported by the tridentate bis(phosphine)phosphido ligand bis(2-diisopropylphosphinophenyl)phosphide) [^{i}Pr–PPP] have been synthesized and characterized (**1–4**). X-Ray structural studies of [^{i}Pr–PPP]PtCl (**1**) and [^{i}Pr–PPP]PtCH$_3$ (**3**) complexes show meridional [^{i}Pr–PPP] ligands around approximately square-planar platinum centers. Structural data and NMR analysis highlight a strong *trans* influence for the phosphido phosphorous donor, comparable to that of the anionic aryl carbon of the classic PCP pincer complexes. A series of thermally stable [PPP]Pt(IV) compounds, including [PPP]Pt(CH$_3$)$_2$X [X = I (**5**) and SbF$_6$ (**6**)], were also synthesized. The study of the binding affinity of SO_2 and NO to complex **1** has also been addressed.

1. Introduction

Transition metal complexes featuring pincer-type ligands constitute a large family of compounds that have been the subject of intense research in recent years. Such complexes play important roles in organometallic reactions, in catalysis, and in the design of new materials, switches, and sensors.[1–4]

The remarkable versatility observed for pincer-based metal complexes is attributable to a balance between their thermal stability and their reactivity patterns, which can be controlled by appropriate ligand modifications and/or variation of the metal center. In such systems, modifications to the ligand architecture are faithfully reflected in the steric and electronic properties of the complexed metal centre, furnishing essential information for rationalizing the relationship between the structure of the organometallic complexes and their chemical behavior.

For this reason, since the initial investigations of cyclometalated phosphine-based pincer complexes (PCP complexes) by Shaw[5] a significant effort has been devoted to the synthesis of structurally and/or electronically related systems where strategic alterations have been introduced into the pincer ligand architecture, including variation of the central donor fragment as well as the ancillary ligand backbone.[6–9] Several variations of the central anionic donor have been explored, but ligands with arylic carbon as the central anionic donor (PCP) remain the most widely used. Such PCP complexes, for their high thermal stability, have been found to support a number of interesting catalytic and stoichiometric transformations such as alkane dehydrogenations[10–13] and C–C bond-forming reactions including Heck couplings,[14,15] as well as allylation reactions with aldehydes.[16]

Anionic pincer-like ligands bearing a combination of soft phosphine and hard π-base amido donors (PNP) were popularized by Fryzuk and coworkers.[17–19] More recently, new platinum group complexes of anionic (PNP) ligands where the *o*-arylene units link the amido and phosphine site have been reported[20–25] and their behavior in N–H and N–C oxidative addition reactions have also been discussed.[26–28] Thermally robust pincer-type bis(8-quinolinyl)amido (BQA) platinum(II)[29] and platinum(IV)[30] complexes have been reported by our own labs, including species that mediate base-promoted[31] and Lewis-acid[30] promoted arene C–H activation reactions.

Peters and coworkers have explored the chemistry of diaryphosphido phosphine [^{i}Pr–PPP] ligands as efficient supports in accommodating different oxidation states of a Cu_2P_2 core.[32] Considering that these ligands are conceptually related to the popular family of the anionic pincer PNP ligands in which the anionic donor of the amide bridge has been substituted with a more electron-releasing phosphide donor, we decided to extend their employment within divalent group 10 chemistry. Our interest in the pincer-type PPP framework is motivated, in part, by the following rationale: these ligands should form very robust square planar complexes with a well-defined geometry in which the additional ligand is forced to occupy a coordination site that is *trans* to a phosphido donor group. The incorporation of a strongly electron-donating and *trans*-labilizing phosphido donor group may promote the formation of coordinatively unsaturated complexes that exhibit interesting reactivity patterns.[33] Furthermore, the phosphido moiety is an electronically flexible donor, as it can serve as an efficient σ and possibly π donor.

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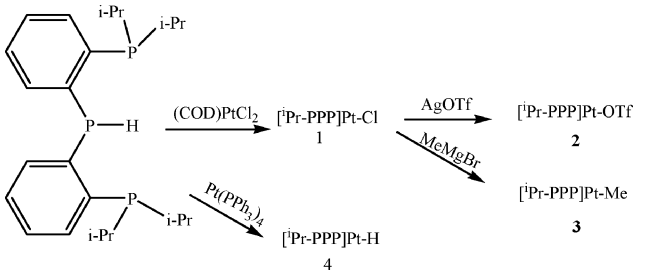
† Electronic supplementary information (ESI) available: ORTEP diagrams of **1** and **3**, fluorescence spectra and ^{31}P-NMR spectrum of **1** upon NO binding and X-ray crystallographic details are reported. CCDC reference numbers 837134 and 837135. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10825e

In this contribution we report the preparation and characterization of divalent platinum complexes of [^{i}Pr–PPP]–H ligand and their reactivity with respect to oxidative addition reactions. The electronic properties of the title complexes have also been explored by studying the binding modes of probes commonly used for this aim (*e.g.* SO_2, NO) by means of NMR, IR and fluorescence spectroscopies.[34]

2. Results and discussion

2.1 Synthesis and characterization of platinum(II) complexes

The ^{i}Pr–PPP–H ligand was synthesized according to the published method.[32] The NMR analysis confirms the C_{2v} symmetry of the ^{i}Pr–PPP–H ligand in solution. The diastereotopicity of the two methyl groups within each isopropyl group is evident in both the ^{1}H and ^{13}C NMR spectra. The reaction between ^{i}Pr–PPP–H and (COD)$PtCl_2$, in THF in the presence of ^{i}$PrEt_2N$ at 50 °C, produced a homogeneous deep orange solution from which complex **1** was isolated in excellent yield (*ca.* 85%) (Scheme 1).



Scheme 1

Solution NMR studies in C_6D_6 indicated that the cyclooctadiene (COD) is easily displaced from (COD)$PtCl_2$ by the [^{i}Pr–PPP]–H ligand upon mixing at room temperature to form a solution of the [^{i}Pr–PPP]-Pt(Cl) complex **1**. ^{1}H and ^{31}P NMR spectra, collected shortly after mixing, showed no build-up of a species containing the P–H functionality. The NMR data are consistent with a square-planar geometry for complex **1** where the [^{i}Pr–PPP] ligand exhibits a meridional coordination mode, as is evident from the presence of a virtual quartet resonance observed for the *o*-phenylene carbon atoms in the ^{13}C NMR spectrum.[35] A C_2 symmetry of the complex in solution can be assumed, consistent with the observation that two resonances are observed for two non equivalent C–H protons of the diasterotopic isopropyl groups.

In the ^{31}P NMR spectrum the two resonances, corresponding to the neutral and anionic phosphorous donors, are strongly shifted downfield from the corresponding ligand precursor. A downfield shift of some 15–25 ppm at the central phosphorus due to metallation and a coordination chemical shift of 20–30 ppm downfield for the flanking phosphorus atoms[37] are expected. A downfield shift of some 115 ppm for the central phosphorus and some 60 ppm for the flanking phosphorus atoms are observed. This can be explained in terms of the ring effect[36,37] whereby the phosphorus atom experiences an additional chemical shift in the ^{31}P-NMR spectrum when the phosphorus is part of a metallacycle. The value of this ring effect is approximately 30–40 ppm downfield for a five-membered ring (platinum). For the flanking phosphorus atoms we expect a downfield shift of 60 ppm (40 ppm ring effect, 20 ppm coordination chemical shift), close to the experimental value of 59.34 ppm. The chemical shift and $^1J_{Pt-P}$ value (2795 Hz) related to the neutral phosphorous atoms are typical of square planar Pt(II) complexes with *trans*-phosphines; comparable values are reported for the analogous [^{i}Pr–PNP] and [^{i}Pr–PCP] platinum complexes.[28,38]

The central phosphorus atom experiences two ring effects as it is part of two five-membered metallacycles. For the central phosphorus atom a 105 ppm downfield (2 × 40 ppm ring effect, 25 ppm coordination chemical shift) is computed, a value close to the experimental value of 115.8 ppm. The small $^1J_{Pt-P}$ coupling constant (1236 Hz) relative to the phosphido phosphorous atom, as previously observed for terminal platinum(II) phosphido complexes,[39] is rationalized in terms of low s-character in the Pt–P bond. This supposition suggests that the phosphido phosphorous atom is pyramidal with a sterochemically active lone pair, and that a planar phosphido donor involved in Pt–P multiple bonding is not present.[40]

Complex **1** is stable in solution and there was no detectable decomposition by NMR spectroscopy after thermolysis in C_6D_6 at 80 °C for 24 h.

Addition of one equivalent of silver triflate Ag(OTf) to a deuterated benzene solution of [^{i}Pr–PPP]Pt(Cl) at room temperature afforded [^{i}Pr–PPP]Pt(OTf) (**2**). The reaction proceeded slowly on the basis of ^{31}P NMR investigations, but after 12 h at 90 °C the conversion of **1** to **2** was quantitative. When the reaction was performed at room temperature in THF-d_8, quantitative formation of complex **2** was observed within a few minutes after mixing. The ^{31}P NMR spectrum for **2** shows a very large value (2659 Hz) for the coupling $^1J_{Pt-P}$ constant relative to the phosphido phosphorous donor, in agreement with the presence of an extremely weak *trans* influencing ligand.

The treatment of complex **1** with CH_3Li in tetrahydrofuran at –78 °C afforded the methyl complex [^{i}Pr–PPP]Pt(CH_3) **3** in *ca.* quantitative yield. Analogous results were obtained by alkylation of **1** with CH_3MgBr under the same reaction conditions. However, a mixture of several products was obtained from the reaction between [^{i}Pr–PPP]H and a suitable precursor that might undergo loss of methane, such as (COD)$PtMe_2$. An attempted metathesis reaction between (COD)PtMeCl and the [^{i}Pr–PPP]Li led to several byproducts.

Similar to the halide analogue, complex **3** is thermally stable at high temperature, and no decomposition was observed when heating at 80 °C for 24 h in C_6D_6 solution, as indicated by NMR spectroscopic data. The methyl ligand in [^{i}Pr–PPP]Pt(CH_3) is unambiguously observed in the ^{13}C NMR spectrum as a doublet of triplets flanked by satellites at –12.0 ppm with a $^2J_{P-C}$ of 37.7 Hz relative to the phosphido donor and a $^2J_{P-C}$ of 7.5 Hz relative to the neutral phosphine donors.

The solution ^{1}H NMR data point out a solution structure characterized by C_{2v} symmetry, as suggested by the presence of a single signal for the C–H isopropyl protons. The presence of the strongly *trans*-influencing methyl group should increase the Pt–P (phosphido) bond distance, allowing for a fast flipping motion of the chelate backbone that would render the axial and equatorial isopropyl groups equivalent on the NMR time scale. In the ^{31}P NMR spectrum the neutral phosphorous donors of **3** exhibit a single resonance that is flanked by ^{195}Pt satellites at 54.0 ppm with a $^1J_{Pt-P}$ of 2843 Hz. These values are in accordance with those

observed for the corresponding chloride complex **1**. The resonance at 78.2 ppm with a $^{1}J_{Pt-P}$ of 648 Hz corresponds to the anionic phosphido donor. The J_{Pt-P} value is lower than that observed for complex **1** because the phosphido donor is now *trans* to a strongly *trans*-influencing methyl group.

The hydride platinum(II) complex **4** was prepared by oxidative addition of P–H in the reaction of the [^{t}Pr–PPP]H ligand with $Pt(PPh_3)_4$ in C_6D_6 and followed by ^{1}H and ^{31}P NMR spectroscopies. The ^{31}P NMR spectrum is very simple and shows a reaction mixture containing the reactants, free PPh_3 and [^{t}Pr–PPP]Pt–H (complex **4**) as the only Pt-containing product. No intermediate species have been detected during the reaction, and a complete conversion to complex **4** is achieved in about 3 h. In the ^{31}P NMR spectrum the neutral phosphorous donors exhibit a resonance, flanked by ^{195}Pt satellites, at 74.32 ppm with a $^{1}J_{Pt-P}$ of 2790 Hz.

The resonance at 68.79 ppm, corresponding to the central phosphorous atom, shows a $^{1}J_{Pt-P}$ of 577 Hz. This value is similar to that observed for the complex [^{t}Pr–PPP]Pt(CH_3), in agreement with the fact that in **4** the phosphido donor is bound to platinum *trans* to a strongly *trans*-influencing hydride ligand. In the ^{1}H NMR spectrum, the resonance of the hydrogen of the Pt–H group is a doublet of triplets (at –0.272 ppm with $^{2}J_{H-P1}$ of 31 Hz and a $^{2}J_{H-P2-3}$ of 7 Hz) flanked by ^{195}Pt satellites with a $^{1}J_{H-Pt}$ of 721 Hz. The $^{1}J_{Pt-H}$ value fits well with values of other known Pt(II) hydrides[28] featuring a ligand *trans*-disposed to the hydride that is likewise strongly *trans*-influencing.[41] Similarly to complexes **1** and **3**, complex **4** is stable in C_6D_6 solution at high temperature (80 °C for 24 h). As for the methyl complex **3**, the solution NMR data point to a highly symmetric solution structure characterized by C_{2v} symmetry due to a fast flipping motion of the chelate backbone.

2.2 X-Ray structural studies

The solid-state structures of **1** and **3** were elucidated by X-ray diffraction studies. Single crystals of **1**, suitable for X-ray diffraction, were grown by vapor diffusion of petroleum ether into a concentrated benzene solution.‡ The solid state structure of complex **1** is illustrated in the X-ray picture (Fig. 1).

The coordination environment around Pt is approximately square planar, as observed for the solution structure determined by NMR spectroscopy. The deviation from the idealized square planar geometry is primarily caused by the chelate PPP constraint with the P(3)–Pt(1)–P(2) angle of 167.414(10)°. The Pt–Cl distance in **1** (2.3963(10) Å) is appreciably longer than that observed in the related [Ph–PNP]PtCl complex[21] (2.318(2) Å) but shorter than that observed in the complex [^{t}Pr–PCP]PtCl (2.436(14) Å),[38] suggesting that the *trans* influence of the phosphido donor is appreciably larger than that of the corresponding amido ligand but less than that of the anionic aryl carbon. The bond distances (2.2573(11) Å) and angles (included between 103.6° and 110.6°) of the phosphido phosphorous atom suggest a pyramidal geometry

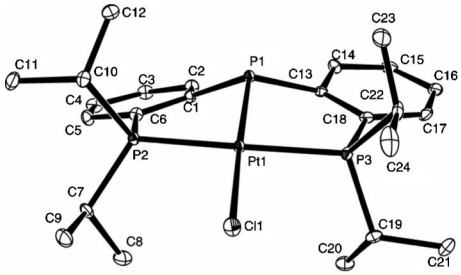


Fig. 1 ORTEP diagram of [^{t}Pr–PPP]PtCl, **1**, with thermal ellipsoids drawn at 30% probability level. The crystal structure of **1** contains two independent molecules in the asymmetric unit. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt(1)–P(1) = 2.2573(11), Pt(1)–P(2) = 2.3107(10), Pt(1)–P(3) = 2.2842(11), Pt(1)–Cl(1) = 2.3963(10). Selected bond angles (deg): P(1)–Pt(1)–P(2) = 84.52(4), P(1)–Pt(1)–P(3) = 85.92(4), P(2)–Pt(1)–Cl(1) = 97.97(4), P(3)–Pt(1)–Cl(1) = 91.92(4).

of the donor atom and are in accordance with the solution structural information deducted from the analysis of the NMR spectra: the phosphorous donor forms a single bond with the platinum centre and retains its stereochemically active lone pair.

Single crystals of **3** suitable for X-ray diffraction studies have been obtained *via* slow evaporation of a petroleum ether solution of the complex. The solid-state structure is represented in Fig. 2. The platinum centre lies on an approximate square plane defined by the four donor atoms with the methyl ligand being *trans* to the phosphido phosphorous atom. The P(3)–Pt(1)–P(2) angle is 161.66(5)° and the Pt–CH_3 distance is 2.157(5) Å. As expected from the greater *trans* influence of Me in comparison to that of Cl, the Pt–P bond in **3** *trans* to the methyl group (2.3091(14) Å) is longer than that *trans* to Cl (2.248 Å).[41] The elongation of this bond involves an increased flexibility of the [^{t}Pr–PPP] ligand around the metal centre, which helps to account for the C_2 symmetry observed for the complex **3** in solution.

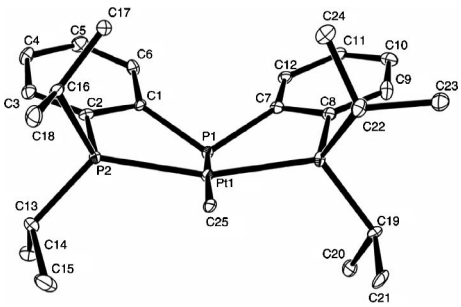


Fig. 2 ORTEP diagram of [^{t}Pr–PPP]PtCH_3, **3**, with thermal ellipsoids drawn at 30% probability level. The crystal structure of **3** contains two independent molecules in the asymmetric unit. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt(1)–P(1) = 2.3091(14), Pt(1)–P(2) = 2.2820(15), Pt(1)–P(3) = 2.2780(15), Pt(1)–C(25) = 2.157(5). Selected bond angles (deg): P(1)–Pt(1)–P(2) = 85.30(5), P(1)–Pt(1)–P(3) = 85.16(5), P(2)–Pt(1)–C(25) = 96.41(15), P(3)–Pt(1)–C(25) = 93.84(15).

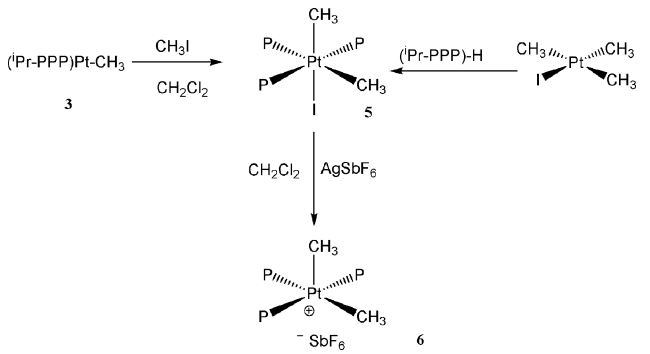
2.3 Oxidative addition reactions

Two-electron oxidative addition to square planar d^8 late transition metal centres represents the key step in a variety of catalytic processes and has been extensively studied[42–45] While copious studies on the oxidative addition have been performed on complexes

‡ *Crystal data for* **1**. Formula: $C_{24}H_{36}ClP_3Pt$, FW = 647.97, monoclinic, space group $P2_1/c$(n. 14), $Z = 8$, $a = 11.612(2)$ Å, $b = 14.046(2)$ Å, $c = 30.941(5)$ Å, $\beta = 92.196(17)°$, $V = 5042.7(14)$ Å^3, $D_x = 1.707$ g cm^{-3}, $\mu_{calc} = 5.871$ mm^{-1}. *Crystal data for* **3**. Formula: $C_{25}H_{39}P_3Pt$, FW = 627.55, monoclinic, space group $P2_1/c$, $Z = 8$, $a = 11.7084(6)$ Å, $b = 13.9668(7)$ Å, $c = 31.1141(16)$ Å, $\beta = 91.280(2)°$, $V = 5086.8(4)$ Å^3, $D_x = 1.639$ g cm^{-3}, $\mu_{calc} = 5.715$ mm^{-1}.

of Pt(II) bearing chelating nitrogen ligands,[46–50] less mechanistic information regarding the corresponding phosphine complexes is available.[51,52] With reference to pincer platinum(II) complexes, according to literature data,[53,54] the oxidative addition of CH_3I to neutral platinum(II) complexes bearing (NCN) ligands does not lead to oxidative addition products that can be isolated. However, the fact that neutral [NCN]PtX platinum complexes react with CH_3I to give the [NCN]PtI suggests the transient formation of Pt(IV) species.[55] Apparently, the subsequent reductive elimination reaction is faster than the corresponding oxidative addition, and hence the proposed platinum(IV) intermediates are not observed. Platinum(IV) complexes containing [NCN] pincer ligands are only obtained using stronger oxidizing agents like X_2 or CuX_2.[56] By contrast, (BQA)PtMe does react favorably with MeI to afford an isolable (BQA)Pt(IV) dimethyl–iodo species.[30] More recently, a series of thermally stable (NSiN)Pt(IV) complexes were reported by Don Tilley *et al.*[57]

We investigated the reactivity of the [^{i}Pr–PPP] platinum complexes in oxidative addition reactions with different reagents because the electron-rich complex **3** is a suitable substrate for these reactions. The oxidative addition of CH_3I to complex **3** proceeded at room temperature, within seconds, in either CH_2Cl_2 or THF solution, to afford the stable [^{i}Pr–PPP]Pt$(CH_3)_2$I (**5**) as illustrated in Scheme 2.



Scheme 2

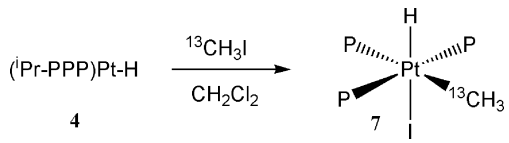
In most cases the oxidative addition of methyl iodide to platinum(II) complexes occurs by the polar S_N2 mechanism and gives *trans* stereochemistry,[58] though subsequent isomerization can give rise to different diastereomers, some of which appear to arise from *cis* oxidative addition.[59] In the case of pincer complexes, the number of possible diastereomers is strongly limited by the constraints imposed by the tridentate ligand, which generally exhibits a strong preference for a meridional coordination mode. For complex **5** the presence of a single species is established from the ^{1}H, ^{31}P and ^{13}C NMR spectra of the complex, obtained rapidly after isolation so as to minimize possible complication due to slow isomerization in solution subsequent to oxidative addition.

The ^{31}P NMR spectrum of **5** exhibits a resonance, flanked by ^{195}Pt satellites at 59.7 ppm with a $^1J_{Pt–P}$ of 2602 Hz and a $^3J_{P–P}$ of 8 Hz for the equivalent neutral phosphorous atoms. The $^1J_{Pt–P}$ value is typical for a *trans* geometry of the neutral phosphine donors, where the lower value is expected due to the increase in coordination number correlating with the rise in the platinum oxidation state.[60] The presence of a single resonance for the two equivalent phosphine donors suggests a meridional arrangement of the [^{i}Pr–PPP] ligand. The signal at 71.1 ppm with a $^1J_{Pt–P}$ of 1537 Hz corresponds to the phosphido phosphorous. The ^{13}C NMR spectrum of **5** exhibits a resonance (–8.6 ppm; $^1J_{Pt–C}$ = 526 Hz) attributable to a methyl group bound to the metal centre. This is consistent with the value of the one-bond Pt–C coupling. An additional resonance attributable to a methyl carbon bound to the metal center is observed at 21.8 ppm. Alternatively, the same product was obtained by reaction of the [^{i}Pr–PPP]–H ligand with the platinum(IV) precursor $(PtMe_3I)_4$ in the presence of ^{i}PrEt$_2$N at room temperature. Formation of **5** involves formal P–H activation at a Pt(IV) centre.

Displacement of iodide from complex **5** might afford a five-coordinated Pt(IV) complex. The investigation of Pt(IV) chemistry, particularly that of five-coordinate Pt(IV) compounds, is important, due to their relevance to Pt(II)-catalyzed C–H activation/functionalization processes.[47,61–63] Despite recent advances in this field, five-coordinate organoplatinum(IV) species remain scarce and challenging to prepare, due to facile reductive elimination processes that regenerate Pt(II). As a result, only a few examples of five-coordinate organoplatinum(IV) compounds have been reported.[64–67]

Addition of one equivalent of silver hexafluoroantimoniate to a methylene chloride solution of [^{i}Pr–PPP]PtMe_2I at room temperature afforded [^{i}Pr–PPP]PtMe_2SbF_6 (**6**) in quantitative yield on the basis of ^{31}P NMR investigation. The complex is thermodynamically stable: no evidence for reductive elimination was obtained upon heating at 80 °C in CD_2Cl_2 solution. Similarly, heating a C_6D_6 solution of complex **6** at 120 °C (bath temperature) resulted in no reaction after 2 days according to the ^{31}P and ^{1}H NMR spectroscopy. This unusual stability of **6** is believed to be due to the ability of the pincer phosphido ligand to stabilize a coordinatively unsaturated, high oxidation state Pt(IV) complex.

The analogous reaction of oxidative addition with isotopically enriched $^{13}CH_3I$ and the pincer platimum hydride complex **4** was performed in CD_2Cl_2 at room temperature and was studied by multinuclear NMR techniques (Scheme 3). In the ^{1}H NMR spectrum a diagnostic Pt(IV)–H signal at –15.65 ppm ($^1J_{Pt–H}$ = 1185 Hz) was observed, this resonance is coherent with the hypothesis that a platinum(IV) methyl hydride complex was formed. A resonance (dd) corresponding to the isotopically enriched methyl group bound to the platinum centre at 1.86 ppm ($^1J_{C–H}$ = 133 Hz, $^2J_{Pt–H}$ = 42 Hz $^3J_{P–H}$ = 10 Hz) was also observed.



Scheme 3

These observations seem to suggest an oxidative addition of methyl iodide to the metal centre. As suggested by a reviewer the methylation of the phosphido P could be a viable reaction with formation of a cationic Pt(II) complex.[69] Further studies are underway to examine this issue.

2.4 Reversible binding of SO_2 and NO to (1)

SO_2 has been shown to be a versatile ligand in inorganic and organometallic chemistry most likely due to the fact that it can

act both as a Lewis base or as an acid. Moreover, since there are several possible binding modes of sulfur dioxide to a metal center, this ligand is considered a model probe for shedding light on the electronic character of a metal center.[68] A wide number of five-coordinate sulfur dioxide adducts of square-planar Pt(II) complexes containing "NCN-pincer" ligands have been reported.[70–74] In these cases, the Pt(II) centers are reported as the nucleophilic sites which easily react with the Lewis acid SO_2.[68] Due to their well-known similarity, SO_2 and NO were our ligands of choice to study binding phenomena to the platinum centre of complex **1**.

Addition of an SO_2 saturated benzene solution to a benzene solution of **1** led to the formation of the corresponding five-coordinate SO_2 adduct. Product formation is immediate on the laboratory time scale. A color change of the complex solution from pale yellow to bright orange is diagnostic for the SO_2 binding process. Subsequent bubbling of argon through the sample solution restored the initial pale yellow color, thus suggesting that removal of SO_2 was occurring. Infrared spectroscopic investigations provided clear evidence for SO_2 adduct formation. When monitoring the benzene solution of the SO_2–Pt complex *via* IR, a signal at 1261 cm^{-1} was found. This signal is characteristic for the asymmetric stretching mode of SO_2 bound to Pt d^8 centers.[75] When comparing the frequency of the asymmetric stretching mode of the SO_2 bound with that of the SO_2 free (1335 cm^{-1}), it results in a shift towards lower values, as already reported in the literature.[77]

SO_2 binding to **1** was also assessed by means of fluorescence. Exciting **1** at its absorption maximum (λ = 300 nm), an emission band centered at 355 nm was obtained. Addition of a considerable excess of SO_2 over the concentration of **1** resulted in a 85% quenching of the fluorescence intensity (see Fig. S3†). When bubbling argon through the sample solution, the fluorescence intensity of **1** was slowly restored. Analogous to the binding of SO_2, NO binding to **1** was studied by fluorescence spectroscopy. The fluorescence intensity of **1** (λ exc = 300 nm; λ em = 355 nm) was quenched upon NO addition (see Fig. S4†).

The SO_2/NO binding to the platinum centre was followed by NMR spectroscopy. The ^{31}P-NMR analysis showed that the reaction of [^{i}Pr–PPP]PtCl with NO or SO_2 resulted in a strong upfield shift of the central phosphorus atom (42.1 ppm for NO and 42.4 ppm for SO_2) and a small upfield shift for the flanking phosphorus atoms (0.1 ppm for NO and 5.3 ppm for SO_2). All signals continued to exhibit $^1J_{Pt-P}$ satellites indicating coordination of the central phosphorus atom to platinum (see Fig. S5 in the Supporting information†). The likely explanation is a weakening of the Pt–P bond of the central phosphorus atom resulting in a significantly reduced ring effect in the phosphorus resonance (upfield shift). The incoming neutral ligand (NO or SO_2) causes the central anionic phosphorus to leave creating a cationic platinum species. The pincer geometry of the [^{i}Pr–PPP]–ligand prevents complete cleavage of the central Pt–P bond resulting in a weakened Pt–P bonding interaction, a reduced ring effect for all three phosphorus atoms and a partial positive charge on platinum. This partial positive charge causes a downfield shift of the strongly coordinated flanking phosphorus atoms whereas the reduced ring effect results in an upfield shift for both phosphorus signals. For the flanking phosphorus atoms, the two effects evidently coincidentally cancel each other. As suggested by fluorescence spectroscopy, bubbling argon through the NMR samples of the NO and SO_2 Pt adducts restores complex **1** according to ^{31}P NMR spectroscopy and establishes a clean and reversible process.

To gain more insight into the mechanism of the SO_2/NO binding processes, ^{31}P NMR experiments of the free ^{i}Pr–PPP–H ligand in the presence of large excesses of either SO_2 or NO gas were undertaken. In both cases, upon gas addition, the ^{31}P NMR spectra of the free ^{i}Pr–PPP–H resulted unchanged. This finding suggests that the binding occurs to the platinum center, as already observed in the PCP complexes described by Van Koten.[75]

3. Conclusions

Several reactions described in this paper have shown that the ^{i}Pr–PPP–H ligand is readily installed *via* reactions of the P–H bond activation at platinum(0) and platinum(II) centers. A related reaction of note involves addition of the ^{i}Pr–PPP–H ligand to the complex $[PtMe_3I]_4$ which involves an activation of the P–H bond at a Pt(IV) center, to form the [^{i}Pr–PPP]$PtMe_2I$ complex **5**. The reactivity of the platinum(II) complexes towards oxidative addition reactions was also investigated.

The electronic character of the platinum center in the platinum(II) complex **1** has been studied by monitoring the binding modes of SO_2 and NO. The reversibility found for the binding of both gases to **1** make it a potential candidate for implementation in a SO_2 and NO sensing device. Fine-tuning of the ligand framework with the aim of changing the electrophilicity of the metal center, in addition to theoretical investigations of the SO_2 and NO binding mechanism, would aid the rational design of new SO_2 and NO sensors. To this end further studies in our laboratory are currently under way.

4. Experimental

4.1 General

All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran to confirm effective oxygen and moisture removal. All the solvents were degassed with nitrogen and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received.

The ^{i}Pr–PPP–H ligand[34] and the complex $Pt(COD)Cl_2$[76] were prepared according to literature procedures.

Elemental analyses were performed by Desert Analytics, Tucson, AZ and by a PERKIN-Elmer 240-C of the microanalytical laboratory of the University of Salerno. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and degassed and dried over activated 3 Å molecular sieves prior to use. The NMR spectra were recorded on a Varian Mercury-300 or INOVA-NMR spectrometer and on a Bruker Avance spectrometer (^{1}H 400 MHz, ^{13}C 100.62 MHz, and ^{31}P 161.97 MHz). Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane and coupling constants (J) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6 and δ 7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced using the

residual solvent peak at δ 128.39 for C_6D_6 and δ 77.23 for $CDCl_3$. ^{19}F and ^{31}P NMR spectra are referenced externally using $CFCl_3$ in $CHCl_3$ at δ 0 and 85% H_3PO_4 at δ 0, respectively.

Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual. X-Ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 837134: [^{i}Pr–PPP]-Pt(Cl) (**1**) and 837135: [^{i}Pr–PPP]-Pt(CH_3) (**3**). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, Union Road, Cambridge, CB2 1EZ, U.K. [fax: (+44)1223-336033, e-mail: deposit@ccdc.cam.ac.uk].

4.2 Synthesis of [^{i}Pr–PPP]PtCl (1)

To a reaction vessel containing (COD)$PtCl_2$ (0.470 g; 1.26 mmol) and ^{i}Pr–PPP–H ligand (0.526 g; 1.26 mmol) dissolved in THF (15 mL), was quickly added, at room temperature, a solution of $HNEt^iPr_2$ (0.321 g, 2.48 mmol) in 2 mL of THF. The solution was stirred at 50 °C for 2 h. The resulting yellow solution was cooled at room temperature and reaction solution volatiles were removed *in vacuo* affording a yellow residue. This crude product was extracted with benzene (15 mL) and filtered through celite on a sintered-glass frit. The solvent was again removed under reduced pressure. The obtained solid was washed with methanol (2 × 3 mL) and, subsequently, with petroleum ether (2 × 5 mL) and then dried *in vacuo* to give the desiderated product as analytically pure compound (yield 92%). Crystals for X-ray analysis were obtained *via* vapor diffusion of petroleum ether into a benzene solution of the complex.

^1H NMR (400 MHz; benzene-d_6): δ 7.88 (dd, 2H, J_{H-H} = 8 Hz, J_{H-H} = 3 Hz, Ar–*H*), 7.13 (m, 2H, Ar–*H*), 7.01 (m, 2H, Ar–*H*), 6.93 (t, 2H, J_{H-H} = 8 Hz, Ar–*H*), 2.85 (m, 2H, C*H*(CH_3)$_2$), 2.43 (m, 2H, C*H*(CH_3)$_2$), 1.46–1.40 (m, 12H, CH(C*H*$_3$)$_2$) 1.05–1.03 (m, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100.6 MHz; benzene-d_6): δ 156.1 (dt, J_{C-P} = 36 Hz, J_{C-P} = 18 Hz, C_{ipso}), 133.6 (dt, J_{C-P} = 23 Hz, J_{C-P} = 19 Hz, C_{ipso}), 131.7 (s, *Ar*), 131.0 (s, *Ar*), 129.8 (dt, *Ar*, J_{C-P} = 14 Hz, J_{C-P} = 11 Hz), 126.2 (m, *Ar* J_{C-P} = 2 Hz), 27.5 (vt, J_{C-P} = 11 Hz, *C*H(CH_3)$_2$), 26.5 (m, 2C, *C*H(CH_3)$_2$), 25.7 (vt, J_{C-P} = 11 Hz *C*H(CH_3)$_2$), 19.2 (m, CH(*C*H$_3$)$_2$), 19.1 (m, CH(*C*H$_3$)$_2$), 18.5 (m, CH(*C*H$_3$)$_2$), 18.4 (m, CH(*C*H$_3$)$_2$). ^{31}P NMR (161.97 MHz; benzene-d_6): δ 68.8 (s, 1P, $^1J_{Pt-P}$ = 1237 Hz), 59.3 (s, 2P, $^1J_{Pt-P}$ = 2796 Hz). Anal. calcd for $C_{24}H_{36}P_3PtCl$: C, 44.48; H, 5.60. Found C, 44.38; H, 5.82.

4.3 Synthesis of [^{i}Pr–PPP]PtOTf (2)

A Teflon-capped J. Young tube was charged with a benzene solution (0.7 mL) of [^{i}Pr–PPP]PtCl (25 mg, 0.039 mmol) and silver triflate (10 mg, 0.039 mmol) at room temperature. The reaction was monitored by ^{31}P NMR spectroscopy which indicated formation of [^{i}Pr–PPP]PtOTf quantitatively in 12 h at 90 °C. An analogue NMR experiment was performed in THF-d_8, in this solvent the product is quantitatively obtained in about 10 min. ^1H NMR (C_6D_6, 400 MHz): δ 8.94 (t, 2H, J_{H-H} = 8 Hz, Ar–*H*), 7.58 (m, 2H, Ar–*H*), 7.10 (m, 2H, Ar–*H*), 6.98 (m, 2H, Ar–*H*), 2.87 (m, 2H, C*H*(CH_3)$_2$), 2.62 (m, 2H, C*H*(CH_3)$_2$), 1.42 (m, 12H, CH(C*H*$_3$)$_2$), 1.03 (m, 12H, CH(C*H*$_3$)$_2$). (THF-d_8, 400 MHz): δ 8.82 (t, 2H, Ar–*H*, J_{H-H} = 8 Hz), 7.94 (m, 2H, Ar–*H*), 7.83 (m, 2H, Ar–*H*), 7.73 (m, 2H, Ar–*H*), 3.44 (m, 2H, C*H*(CH_3)$_2$), 3.07 (dd, 2H, J_{H-H} = 8 Hz, J_{P-H} = 10 Hz, C*H*(CH_3)$_2$), 1.48 (m, 6H, CH(C*H*$_3$)$_2$), 1.33 (m, 12H, CH(C*H*$_3$)$_2$) 1.11 (dd, 6H, J_{H-H} = 8 Hz, J_{P-H} = 10 Hz, CH(C*H*$_3$)$_2$). ^{31}P NMR (C_6D_6, 161.97 MHz) δ 75.70 (s, 1P, $^1J_{P-Pt}$ = 2659 Hz), 70.16 (s, 2P, $^1J_{P-Pt}$ = 2682 Hz), (THF-d_8, 161.975 MHz), δ 72.20 (s, 2P, $^1J_{P-Pt}$ = 2745 Hz), 66.24 (s, 1P, $^1J_{P-Pt}$ = 2709 Hz), ^{13}C NMR (C_6D_6, 100.61 MHz): δ 151.3 (t, $^1J_{C-P}$ = 15 Hz, C_{ipso}), 147.3 (t, $^1J_{C-P}$ = 19 Hz, C_{ipso}), 133.6 (m, *Ar*), 132.6 (s, *Ar*), 131.8 (d, *Ar*, $^1J_{C-P}$ = 17 Hz), 26.4 (t, $^1J_{C-P}$ = 18 Hz, *C*H(CH_3)$_2$), 24.2 (t, $^1J_{C-P}$ = 19 Hz, *C*H(CH_3)$_2$), 19.2 (s, CH(*C*H$_3$)$_2$), 18.0 (s, CH(*C*H$_3$)$_2$), 16.8 (s, CH(*C*H$_3$)$_2$), 16.4 (s, CH(*C*H$_3$)$_2$), 14.0 (s, Pt–SO_3CF_3), ^{19}F NMR (THF-d_8, 376 MHz) = δ –80.83 (s, Pt–SO_3CF_3).

Anal. calcd for $C_{25}H_{36}P_3PtSO_3F_3$: C, 39.43; H, 4.76. Found C, 39.80; H, 4.82.

4.4 Synthesis of [^{i}Pr–PPP]PtMe (3)

Complex **1** (0.900 g, 1.39 mmol) was dissolved in THF (15 mL) and the resulting yellow solution was cooled at –78 °C. A diethyl ether solution (1.6 M) of MeLi (1.53 mmol) was diluted in 2 mL of diethyl ether and added to the THF solution of complex 1 at –78 °C. The resulting orange solution was stirred at –78 °C for 30 min. and then slowly warmed at room temperature and stirred for an additional 1 h. The reaction solution volatiles were removed *in vacuo* affording a yellow brown residue. This product was extracted in benzene and filtered thought celite. An analytically pure product was obtained by crystallization from petroleum ether at low temperature. Crystals for X-ray analysis were obtained *via* slow evaporation vapor of a solution petroleum ether of the complex. ^1H NMR (300 MHz, benzene-d_6): δ 8.21(dd, 2H, J_{H-H} = 7 Hz, J_{H-H} = 2 Hz, Ar–*H*), 7.12 (m, 4H, Ar–*H*), 6.91 (t, 2H, J_{H-H} = 7 Hz, Ar–*H*), 2.54 (m, 4H, C*H*(CH_3)$_2$), 1.20 (dd, 12H, $^2J_{P-H}$ = 16 Hz and J_{H-H} = 7 Hz, CH(C*H*$_3$)$_2$), 1.09 (dd, 12H, $^2J_{P-H}$ = 16 Hz and J_{H-H} = 7 Hz, CH(C*H*$_3$)$_2$), the Pt*CH*$_3$ signal is obscured under the P(CH(C*H*$_3$)$_2$ signal pattern. ^{13}C NMR (75.409 MHz, benzene-d_6): δ 159.3 (dt, J_{P-C} = 51 Hz, J_{C-P} = 14 Hz, C_{ipso}), 147.3 (t, J_{P-C} = 41 Hz, J_{P-C} = 12 Hz, C_{ipso}); 135.52 (s, *Ar*), 131.7 (s, *Ar*), 130.4 (s, *Ar*),126.0 (s, *Ar*), 26.07 (vt, J_{P-C} = 11 Hz, *C*H(CH_3)$_2$), 19.70 (m, CH(*C*H$_3$)$_2$), 18.62 (m, CH(*C*H$_3$)$_2$), –11.9 (dt, J_{P-C} = 45 Hz, J_{P-C} = 8 Hz, J_{Pt-C} = 582 Hz, Pt–*C*H$_3$). ^{31}P NMR (121.4 MHz, benzene-d_6): δ 78.16 (s, 1P, $^1J_{Pt-P}$ = 648 Hz), 54.02 (s, 2P, $^1J_{Pt-P}$ = 2843 Hz). Anal. calcd for $C_{25}H_{39}P_3Pt$: C, 47.85; H, 6.26; Found: C, 47.22; H, 5.91.

4.5 Synthesis of [^{i}Pr–PPP]PtH (4)

A Teflon-capped J. Young tube was charged with a benzene solution (0.7 mL) of [^{i}Pr–PPP]–H ligand and (31.1 mg, 25 µmol) and $Pt(PPh_3)_4$ (10 mg, 25 µmol) at room temperature. ^1H NMR (300 MHz, benzene-d_6): δ 7.75 (dd, 2H, J_{H-H} = 8 Hz, J_{H-H} = 3 Hz, Ar–*H*), 7.12–7.01 (m, 4H, Ar–*H*), 6.93 (t, 2H J_{H-H} = 8 Hz, Ar–*H*), 2.19 (m, 4H, C*H*(CH_3)$_2$), 1.27 (dd, 12H, J_{H-H} = 8 Hz, CH(C*H*$_3$)$_2$), 0.87 (dd, 12H, J_{H-H} = 7 Hz, CH(C*H*$_3$)$_2$), –0.27 (dt, 1H, $^1J_{Pt-H}$ = 961 Hz, $^2J_{P-H}$ = 77 Hz, $^2J_{P-H}$ = 17 Hz, Pt–*H*). ^{13}C NMR (110.619 MHz, benzene-d_6): δ 160.41 (m, C_{ipso}), 138.42 (d, J_{P-C} = 10 Hz, *Ar*), 136.09 (m, C_{ipso}), 132.75 (d, J_{P-C} = 10 Hz, C, *Ar*), 131.44 (m, *Ar*), 124.94 (s, *Ar*), 25.2 (vt, J_{P-C} = 6 Hz, *C*H(CH_3)$_2$),

24.7 (vt, J_{P-C} = 5 Hz, $CH(CH_3)_2$), 20.2 (m, $CH(CH_3)_2$), 18.8 (bs, $CH(CH_3)_2$). ^{31}P NMR (C_6D_6, 161.975 MHz) δ 72.35 (s, 2P, $^1J_{P-Pt}$ = 2790 Hz), 68.79 (s, 1P, $^1J_{P-Pt}$ = 576 Hz).

Anal. calcd for $C_{24}H_{37}P_3Pt$: C, 46.98; H, 6.08. Found C, 46.76; H, 5.97.

4.6 Synthesis of [^{i}Pr–PPP]PtMe$_2$I (5)

Method (a): To a solution of **3** [^{i}Pr–PPP]PtCH$_3$ (0.200 g, 0.319 mmol) in THF (10 mL) was added CH_3I (0.048 g, 0.342 mmol) and the resulting solution was stirred at room temperature for 2 h. After 2 h a pale yellow solid was observed in suspension. Diethyl ether (5 mL) was added to complete the precipitation of the desiderate product which was separated, washed with ether, and dried under vacuum. Yield 0.200 g, 76%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.59 (m, 2H, Ar–*H*), 6.96 (m, 6H, Ar–*H*) 2.24 (m, 2H, C*H*(CH_3)$_2$), 2.10 (m, 2H, C*H*(CH_3)$_2$)), 1,72 (d, 3 H, $^2J_{Pt-H}$ = 46 Hz, J_{P-H} = 9 Hz Pt–CH_3, the unusually low value of $^2J_{(Pt-H}$ is consistent with the very high *trans* influence of the phosphido donor), 0.96 (m, 12H, CH(C*H*$_3$)$_2$), 0.24 (m, 12H, CH(C*H*$_3$)$_2$). ^{31}P NMR (121.4 MHz, CD_2Cl_2): δ 77.56 (t, 1P, $^1J_{Pt-P}$ = 1559 Hz, $^3J_{P-P}$ = 7 Hz), 65.97 (d, 2P, $^1J_{Pt-P}$ = 2598 Hz). ^{13}C NMR (75.47 MHz, CD_2Cl_2): δ 142.3 (dt, J_{P-C} = 53 Hz, J_{P-C} = 14 Hz, C_{ipso}), 140.0 (dt, J_{P-C} = 41 Hz, J_{P-C} = 23 Hz, C_{ipso}), 134.0–133.3 (m, *Ar*), 28.3 (m *C*H(CH_3)$_2$), δ 25.7 (m, *C*H(CH_3)$_2$), 21.8 (dt, P–*C*H$_3$, J_{C-P} = 35 Hz, J_{C-P} = 10 Hz), 20.0 (t, CH(*C*H$_3$)$_2$, $^2J_{P-C}$ = 20 Hz), 19.2 (m, CH(*C*H$_3$)$_2$), 18.6 (m, CH(*C*H$_3$)$_2$), –8.6 (dt, $^1J_{Pt-C}$ = 526 Hz, J_{P-C} = 78 Hz, J_{P-C} = 8 Hz, Pt–*C*H$_3$).

Method (b): To a solution of Pt(CH$_3$)$_3$I complex (0.175 g, 0.478 mmol) in THF (10 mL) was added a THF (5 mL) solution of the [^{i}Pr–PPP]–H ligand (0.200 g, 0.478 mmol) and 0.0902 g, 0.698 mmol of NEt$_2$^{i}Pr. The resulting solution was stirred at room temperature for 2 h. After 2 h a pale yellow solid was observed in suspension. Diethyl ether (2 mL) was added to complete the precipitation of the desiderate product which was separated, washed with ether, and dried under vacuum. Yield 0.302 g, 82%. Anal. calcd for $C_{26}H_{42}IP_3Pt$: C, 40.58; H. 5.50. Found: C, 40.75; H, 5.37.

4.7 Synthesis of [^{i}Pr–PPP]PtMe$_2$SbF$_6$ (6)

A Teflon-capped J. Young tube was charged with a CD_2Cl_2 solution (0.7 mL) of [^{i}Pr–PPP]PtMe$_2$I (25 mg, 0.039 mmol) and silver hexafluoroantimoniate (10 mg, 0.039 mmol) at room temperature. The reaction was monitored by ^{31}P NMR spectroscopy which indicated formation of [^{i}Pr–PPP]PtMe$_2$ SbF$_6$ quantitatively in 1 h. To remove the AgI salt which had formed, the suspension was filtered. The resulting solution was analyzed *via* NMR.

^{1}H NMR (300 MHz; CD_2Cl_2): δ 8.37 (t, 2H, Ar–*H*, J_{H-H} = 8 Hz), 7.87–7.75 (m, 4H, Ar–*H*), 7.70 (t, 2H, Ar–*H*, J_{H-H} = 5 Hz), 3.03 (m, 2H, C*H*(CH_3)$_2$), 2.88 (m, 2H, C*H*(CH_3)$_2$), 1,78 (d, 3 H, $^2J_{Pt-H}$ = 43 Hz, J_{P-H} = 9 Hz), 1.38 (dd, *J* = 16.5 and 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.30 (dd, *J* = 16.5 and 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09 (dd, 12H, CH(C*H*$_3$)$_2$), the PtC*H*$_3$ signal is obscured under the P(CH(C*H*$_3$)$_2$ signal pattern. ^{31}P NMR (161.97 MHz; CD_2Cl_2): δ 71.23 (t, 1P, $^1J_{Pt-P}$ = 1541 Hz,J_{P-P} = 7 Hz), 59.77 (d, 2P, $^1J_{Pt-P}$ = 2600 Hz). ^{13}C NMR (100.62 MHz; CD_2Cl_2): δ 141.7 (dt, J_{P-C} = 53 Hz, J_{P-C} = 14 Hz, C_{ipso}-P), 139.6 (dt, J_{P-C} = 41 Hz, J_{P-C} = 24 Hz, C_{ipso}–P), 133.1–132.9 (m, *Ar*), 131.9 (td, J_{C-P} = 8 Hz, J_{C-P} = 2 Hz, *Ar*), 27.6 (t, J_{C-P} = 15 Hz, *C*H(CH_3)$_2$), 25.7 (td, *C*H(CH_3)$_2$, J_{C-P} = 16 Hz, J_{C-P} = 3 Hz), 21.0 (dt, Pt–*C*H$_3$, $^2J_{Pt-C}$ = n.d., J_{P-C} = 34 Hz, J_{P-C} = 7 Hz). 19.1 (dt, J_{P-C} = 7 Hz, CH(*C*H$_3$)$_2$), 18.5 (m, 2C, CH(*C*H$_3$)$_2$), 17.5 (t, CH(*C*H$_3$)$_2$, $^2J_{C-P}$ = 6 Hz), 17.5 (t, $^2J_{C-P}$ = 14 Hz, CH(*C*H$_3$)$_2$), –8.0 (dt, Pt–*C*H$_3$, $^1J_{Pt-C}$ = 526 Hz, $^2J_{P-C}$ = 77 Hz, $^2J_{P-C}$ = 7 Hz).

4.8 Synthesis of [^{i}Pr–PPP]PtH*MeI (7)

A small sample (20 mg) of complex 4 was dissolved in CD_2Cl_2 and an excess of methyl iodide was added in a sealed NMR tube. The reaction was followed by ^{1}H and ^{31}P NMR.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.98 (t, 2H, J_{H-H} = 8 Hz, Ar–*H*), 7.96 (m, 4H, Ar–*H*) 3.57 (m, 2H, C*H*(CH_3)$_2$), 3.26 (m, 2H, C*H*(CH_3)$_2$)), 1.86 (dd, 3H, $^1J_{C-H}$ = 133 Hz, $^2J_{Pt-H}$ = 42 Hz, $^3J_{P-H}$ = 10 Hz, Pt–*CH_3) 1,54 (dd, 6 H, J_{P-H} = 18 Hz, J_{H-H} = 7 Hz) 0.98 (m, 6H, CHC*H*$_3$)$_2$), 1.34 (dd, 6H, J_{P-H} = 15 Hz, J_{H-H} = 7 Hz CH(C*H*$_3$)$_2$), 1.15 (m, 12H, CH(C*H*$_3$)$_2$), –15.65 ppm (bs, $^1J_{Pt-H}$ = 1185 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2): 64.3 ppm (s, 2P, $^1J_{Pt-P}$ = 2748 Hz), 113.9 ppm (d, 1P, $^1J_{Pt-P}$ = 1872 Hz, $^1J_{P-C}$ of 42 Hz)

4.9 SO_2 saturated solutions

Saturated solutions of sulphur dioxide (SO_2) were prepared by bubbling SO_2 gas, produced *in situ* according to literature procedures,[77] through 5 mL of dried solvents for periods of up to 1 h.

4.10 Absorbance and fluorescence measurements

Fluorescence spectra were measured on a Cary Eclipse Spectrophotometer in a 10 × 10 mm^2 airtight quartz fluorescence cuvette (Hellma Benelux bv, Rijswijk, Netherlands). Fluorescence measurements were performed in benzene solutions at room temperature. For the SO_2 titrations, the cuvette was filled with benzene sample solutions, after which µL amounts of an SO_2-saturated benzene solution ([SO_2] = 2 M) [78] were injected.

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